BCS Superconductivity of Dirac Electrons in Graphene Layers

N. B. Kopnin[1,2] and E. B. Sonin[3]

[1]*Low Temperature Laboratory, Helsinki University of Technology, P.O. Box 2200, FIN-02015 HUT, Finland*
[2]*L. D. Landau Institute for Theoretical Physics, 117940 Moscow, Russia*
[3]*The Racah Institute of Physics, Hebrew University of Jerusalem, Israel*

(Received 27 March 2008; published 20 June 2008)

Possible superconductivity of electrons with the Dirac spectrum is analyzed using the BCS model. We calculate the critical temperature, the superconducting energy gap, and the supercurrent as functions of the doping level and of the pairing interaction strength. Zero doping is characterized by the existence of a quantum critical point such that the critical temperature vanishes below some finite value of the interaction strength. However, the critical temperature remains finite for any nonzero electron or hole doping level when the Fermi energy is shifted away from the Dirac point. As distinct from usual superconductors, the supercurrent density is not proportional to the number of electrons but is strongly decreased due to the presence of the Dirac point.

DOI: 10.1103/PhysRevLett.100.246808 PACS numbers: 73.63.−b, 74.25.Jb, 74.78.Na

Graphite has attracted the attention of experimentalists and theorists for a long time. The interest is explained by the unusual properties of this quasi-two-dimensional material, which are mostly related to the existence of a Dirac or conic point in the electronic spectrum (see Fig. 1). Though the theory predicted the existence of such a point in graphite many decades ago [1], only recently has experimental evidence of its existence been obtained: first in graphite [2], which is believed to be a stack of weakly coupled atomic layers, and soon after it in graphene [3,4]. The latter discovery has triggered an avalanche of experimental and theoretical works. Moreover, graphene can display unusual properties as a part of normal-superconducting hybrid structures: For example, the Andreev reflection has been predicted to have new features not characteristic for typical contacts [5].

Thorough investigation of graphite has revealed also evidence of intrinsic superconductivity in doped samples (see Refs. [6,7], and references therein). Various mechanisms of superconductivity in graphene have been considered theoretically. Phonon- and plasmon-mediated mechanisms were discussed in Ref. [8], whereas resonating valence bond and density wave lattice models were proposed in Refs. [9–11]. The Cooper pairing in undoped graphene may experience problems because the Fermi surface shrinks near the Dirac point and reduces to zero the number of states at the Fermi energy. Indeed, it was shown within the BCS model [10,12] that the superconducting transition in undoped graphene possesses a quantum critical point at a finite interaction strength below which the critical temperature vanishes. However, one would expect that the electrons in graphene may become unstable towards formation of Cooper pairs for any finite pairing interaction if doping shifts the Fermi level away from the Dirac point, because the behavior of electrons in the latter case bears more resemblance to that in usual metals. This idea has been discussed in Refs. [8,10,13] and verified within the resonating valence bond model in Ref. [9].

The aforementioned investigations of superconductivity in graphene or graphite (except for Ref. [12], where only the undoped case was considered) were done by taking into account the specific details of each particular pairing mechanism. However, it would be worthwhile to perform the analysis in a more general form independent of a particular nature of the pairing mechanism. In the present Letter, we apply the standard *s*-wave BCS model for the Dirac spectrum of electrons with a minimum number of parameters characterizing the pairing interaction, i.e., its intensity and the range of interaction in the momentum space, which may vary depending on the mechanism. Such an approach ignores some details and thus is less accurate. However, we hope that the loss of accuracy is compensated by a more general and transparent picture of the most essential features of the Cooper pairing in systems with the Dirac spectrum.

In what follows, we calculate the critical temperature, the superconducting energy gap, and the supercurrent as functions of the doping level and the pairing interaction strength. Without doping, the critical temperature vanishes

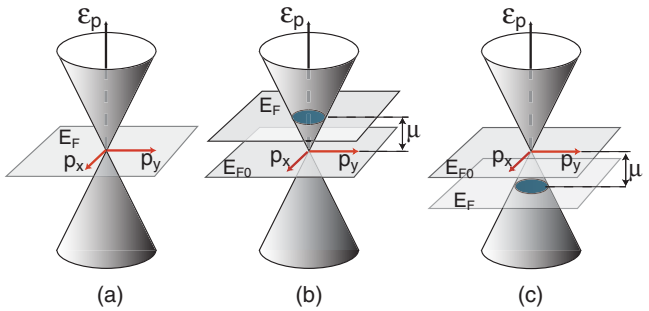

FIG. 1 (color online). Conical energy spectrum. (a) Undoped, (b) electron-doped, and (c) hole-doped spectrum.

below some finite value of the interaction strength. However, the critical temperature is nonzero for any nonzero electron or hole doping level when the Fermi energy is shifted from the Dirac point of the normal-state electronic spectrum. This confirms some earlier results of Refs. [8–13]. At the same time we demonstrate that, in contrast to the previous analysis [10], the supercurrent and thus the Meissner effect do not vanish at $T = 0$ for zero doping. We also show that, as distinct from the usual superconductors, the supercurrent density is not proportional to the total number of electrons but is drastically decreased due to the presence of the Dirac point. Finally, we estimate characteristic length scales (penetration depth and coherence length), relevant for determination of the critical magnetic fields.

Consideration of a two-dimensional model requires a few comments concerning the applicability of the mean-field approach. It is well known that the superfluid transition in a two-dimensional system occurs in the form of the Berezinskii-Kosterlitz-Thouless transition at a temperature lower than the mean-field transition temperature. Thus our calculations provide the upper bound for the transition temperature [9]. Moreover, the applicability of the mean-field approach improves for graphite, where a nonzero interplanar coupling is always present.

Spectrum.—Normal excitations in graphene can be described by two-component wave functions corresponding to two sites in the Brillouin zone [14]. For zero magnetic fields, this approach leads to the effective normal-state energy spectrum

$$\epsilon_{\mathbf{p}} = \pm v_F \sqrt{p_x^2 + p_y^2} + E_{F0}.$$

The two signs refer to the conduction or the valence band, respectively; E_{F0} is the Fermi energy without doping when the Dirac point lies at the Fermi level. We will use this spectrum as a basis for our model assuming that the two sites in the Brillouin zone are equivalent. Doping shifts the Fermi energy by some amount μ, $E_F = E_{F0} + \mu$ (see Fig. 1). The energy measured from the Fermi level is

$$\xi_{\mathbf{p}} = \epsilon_{\mathbf{p}} - E_F = \pm v_F p - \mu.$$

The group velocity is $d\xi_{\mathbf{p}}/d\mathbf{p} = \pm v_F \mathbf{n}$, where $\mathbf{n} = \mathbf{p}/p$. For electron doping $\mu > 0$, we have

$$p = \begin{cases} -(\xi_{\mathbf{p}} + \mu)/v_F, & \xi_{\mathbf{p}} < -\mu, \\ (\xi_{\mathbf{p}} + \mu)/v_F, & -\mu < \xi_{\mathbf{p}}. \end{cases} \tag{1}$$

Similar relations hold for hole doping $\mu = -|\mu|$, as well.

BCS gap equation.—We use the standard BCS theory and assume an s-wave pairing interaction $V_p = -|V_p|$, where $|V_p| \sim |V|a^2$ is the Fourier transform of the pairing potential, V is the energy amplitude, and a is the range of interaction. We do not consider here the nature of pairing interaction but refer the reader to Refs. [8–11,13,15], where various possible mechanisms are discussed. The coupling constant λ is introduced through the equation

$$\frac{|V_p|}{2\pi\hbar^2 v_F^2} = \begin{cases} \lambda/\xi_m, & |\xi_{\mathbf{p}}| < \xi_m, \\ 0, & |\xi_{\mathbf{p}}| > \xi_m. \end{cases}$$

Here ξ_m determines the range of the attractive interaction. We assume that $\xi_m \ll \hbar v_F/a$, where a is the interatomic distance, and consider the low doping limit $|\mu| < \xi_m$.

The Bogoliubov–de Gennes equations in our model are

$$\xi_{\hat{\mathbf{p}}} u + \Delta v = E u, \qquad -\xi_{\hat{\mathbf{p}}} v + \Delta^* u = E v, \tag{2}$$

where $\hat{\mathbf{p}} = -i\hbar\nabla$. The BCS gap equation in a spatially uniform case is

$$1 = \frac{1}{2} \int |V_p| \frac{d^2 p}{(2\pi\hbar)^2} \frac{1}{E_{\mathbf{p}}} [1 - 2n(E_{\mathbf{p}})], \tag{3}$$

where the energy of excitations is $E_{\mathbf{p}} = \sqrt{\xi_{\mathbf{p}}^2 + \Delta^2}$, the phase volume is $d^2 p = p dp d\phi$, where ϕ is the azimuthal angle of $\mathbf{n}$, and $n(E_{\mathbf{p}})$ is the equilibrium Fermi distribution of quasiparticles with energies $E_{\mathbf{p}}$. For zero temperature, the BCS gap equation yields

$$\frac{\xi_m}{\lambda} = \sqrt{\xi_m^2 + \Delta_0^2} - \sqrt{\mu^2 + \Delta_0^2} + |\mu| \ln\left[\frac{|\mu| + \sqrt{\mu^2 + \Delta_0^2}}{\Delta_0}\right] \tag{4}$$

for both electron and hole doping. For $\mu = 0$,

$$\Delta_0 = \xi_m(\lambda^2 - 1)/2\lambda. \tag{5}$$

Nonzero Δ_0 is possible only for the strong-coupling limit $\lambda > 1$ [10,12]. However, Eq. (4) shows that, for a finite doping, a finite Δ_0 exists even in the weak-coupling limit $\lambda < 1$. In the case of a low doping level when Δ_0 is small, Eq. (4) gives the gap in a BCS form

$$\Delta_0 = 2|\mu| \exp\left(-\frac{\xi_m}{|\mu|} \frac{1 - \lambda}{\lambda} - 1\right) \tag{6}$$

with the prefactor determined by the doping level $|\mu|$ rather than by the range of interaction.

Temperature dependence.—For a finite temperature, Eq. (3) yields the gap equation [10]

$$\frac{\xi_m}{\lambda} = 2T \ln\left[\frac{\cosh(\sqrt{\xi_m^2 + \Delta^2}/2T)}{\cosh(\sqrt{\mu^2 + \Delta^2}/2T)}\right] + |\mu| \int_0^{|\mu|} \tanh\frac{\sqrt{\xi^2 + \Delta^2}}{2T} \frac{d\xi}{\sqrt{\xi^2 + \Delta^2}}. \tag{7}$$

For $T \to 0$ we return to Eq. (4). Equation (7) leads to the equation for the critical temperature

$$\Phi(\xi_m/2T_c; \lambda) = F(|\mu|/2T_c), \tag{8}$$

where

$$\Phi(y;\lambda) = \lambda^{-1} y - \ln(\cosh y),$$

$$F(x) = x\int_0^x (x')^{-1}\tanh x' dx' - \ln(\cosh x),$$

and $F(x) > 0$. The critical temperature found from Eq. (8) is plotted in Fig. 2.

For $\mu = 0$, the critical temperature satisfies $\Phi(\xi_m/2T_c;\lambda) = 0$, i.e.,

$$\xi_m/\lambda = 2T_c \ln[\cosh(\xi_m/2T_c)]. \tag{9}$$

This equation has a solution only for an interaction strength above the quantum critical point $\lambda > 1$ (see Fig. 2). If $\lambda \to 1$, we have $T_c = \xi_m(\lambda - 1)/2\ln 2$, which vanishes at $\lambda = 1$. By comparing this with Eq. (5), we find that $\Delta_0 = T_c 2\ln 2$. In the other limit $\lambda \gg 1$, we find that $T_c = \xi_m\lambda/4$ and $\Delta_0 = 2T_c$. These results agree with Ref. [12], where only the undoped case was considered.

However, for any low but finite doping level, the critical temperature is finite. Consider weak-coupling limit $\lambda \ll 1$, where we expect $T_c \ll \mu$. Indeed, the left-hand side of Eq. (8) is $\Phi(y;\lambda) = y(\lambda^{-1} - 1) + \ln 2$ already for $T_c \ll \xi_m$. On the other hand, for $x \gg 1$ the right-hand side of Eq. (8) is

$$F(|\mu|/2T_c) = \frac{|\mu|}{2T_c}\ln\left[\frac{2|\mu|\gamma}{e\pi T_c}\right] + \ln 2, \tag{10}$$

where $\gamma = e^C = 1.78$ and $C = 0.5772$ is the Euler constant. This yields

$$T_c = \frac{2|\mu|\gamma}{\pi}\exp\left[-\frac{\xi_m(1-\lambda)}{\mu\lambda} - 1\right], \tag{11}$$

resulting in the BCS relation $\Delta_0 = (\pi/\gamma)T_c = 1.76T_c$.

Consider the vicinity of the quantum critical point $\mu = 0$ and $\lambda = 1$. On the weak-coupling side $\lambda < 1$, the critical temperature is given by Eq. (11), which is exact provided that $T_c \ll |\mu|$, i.e., for $1 - \lambda \gg |\mu|/\xi_m$. For $|\mu|/\xi_m \sim 1$ and $\lambda \to 1$, Eq. (11) works also reasonably well. For example, Eq. (11) gives $T_c \approx 0.42|\mu|$ for $\lambda = 1$. This can be compared to the exact value for $\lambda = 1$, which is found from the condition $F(|\mu|/2T_c) = \ln 2$ resulting in $T_c \approx 0.40|\mu|$. In the limit $\mu \ll T_c \ll \xi_m$, which is more appropriate on the strong-coupling side of the quantum critical point,

$$T_c = \frac{\xi_m(\lambda-1) + \sqrt{\xi_m^2(\lambda-1)^2 + \mu^2 2\ln 2}}{4\ln 2}.$$

This holds for $|\mu|/\xi_m \ll \lambda - 1 \ll 1$ but also matches with the exact T_c by the order of magnitude when $\lambda \to 1$.

Therefore we come to the conclusion that a finite T_c does always exist for a finite μ. If $\lambda \gtrsim 1$, the critical temperature is close to that determined by Eq. (9) as long as $\mu \ll \xi_m$. If $\lambda \lesssim 1$, we essentially have Eq. (11).

Supercurrent.—Let us assume a homogeneous flow of the condensate: $\Delta = |\Delta|e^{i\mathbf{k}_s\mathbf{r}}$, where $\mathbf{k}_s = \nabla\chi$ is a constant gradient of the order-parameter phase. Consider the state described by the particlelike and holelike Bogoliubov–de Gennes wave functions

$$u(\mathbf{r}) = u_{\mathbf{p}} e^{i\mathbf{p}_+\cdot\mathbf{r}/\hbar}, \qquad v(\mathbf{r}) = v_{\mathbf{p}} e^{i\mathbf{p}_-\cdot\mathbf{r}/\hbar}, \tag{12}$$

where $\mathbf{p}_\pm = \mathbf{p} \pm \hbar\mathbf{k}_s/2$,

$$E_{\mathbf{p}} = E_D + E_{\mathbf{p}}^{(0)}, \qquad E_{\mathbf{p}}^{(0)} = \sqrt{\tilde{\xi}_{\mathbf{p}}^2 + |\Delta|^2}.$$

Here $\tilde{\xi}_{\mathbf{p}} = (\xi_{\mathbf{p}_+} + \xi_{\mathbf{p}_-})/2$, and $E_D = (\xi_{\mathbf{p}_+} - \xi_{\mathbf{p}_-})/2$ is the Doppler energy. The coherence factors

$$u_{\mathbf{p}} = \frac{1}{\sqrt{2}}(1 + \tilde{\xi}_{\mathbf{p}}/E_{\mathbf{p}}^{(0)})^{1/2}, \qquad v_{\mathbf{p}} = \frac{1}{\sqrt{2}}(1 - \tilde{\xi}_{\mathbf{p}}/E_{\mathbf{p}}^{(0)})^{1/2}$$

are found from Eq. (2). The standard expression for the current is

$$\mathbf{j} = 2e\sum_{\mathbf{p}}\left[\frac{\partial\xi_{\mathbf{p}_+}}{\partial\mathbf{p}}|u_{\mathbf{p}}|^2 n(E_{\mathbf{p}}) - \frac{\partial\xi_{\mathbf{p}_-}}{\partial\mathbf{p}}|v_{\mathbf{p}}|^2[1 - n(E_{\mathbf{p}})]\right].$$

In the linear response regime, $E_D = (d\xi_p/d\mathbf{p})\hbar\mathbf{k}_s/2$ and $\tilde{\xi}_{\mathbf{p}} = \xi_{\mathbf{p}}$. By expanding the current in small $E_D \ll \Delta, T$ and making a shift of the momenta in the sum over the states, we find for the two-dimensional current density that

$$\mathbf{j} = e\int\frac{d^2p}{4\pi^2\hbar}\frac{\partial\xi_{\mathbf{p}}}{\partial\mathbf{p}}\left\{2[n(E_{\mathbf{p}}) - n(E_{\mathbf{p}}^{(0)})] + \left(\frac{\partial\xi_{\mathbf{p}}}{\partial\mathbf{p}}\cdot\mathbf{k}_s\right)\frac{\partial}{\partial\xi_{\mathbf{p}}}\left[\frac{\xi_{\mathbf{p}}}{2E_{\mathbf{p}}^{(0)}}[1 - 2n(E_{\mathbf{p}}^{(0)})]\right]\right\}. \tag{13}$$

This yields the current $\mathbf{j} = (e\Lambda/4\pi\hbar)\mathbf{k}_s$, where we have for zero temperature

$$\Lambda = 2|\Delta| + \frac{\mu^2}{\sqrt{\mu^2 + |\Delta|^2}} - \frac{|\Delta|^2}{\sqrt{\mu^2 + |\Delta|^2}}. \tag{14}$$

In contrast to the usual superconductors, the supercurrent density is not proportional to the total electron density, being drastically affected by the presence of the Dirac point. In particular, for weak-coupling limit $|\Delta| \ll \mu$,

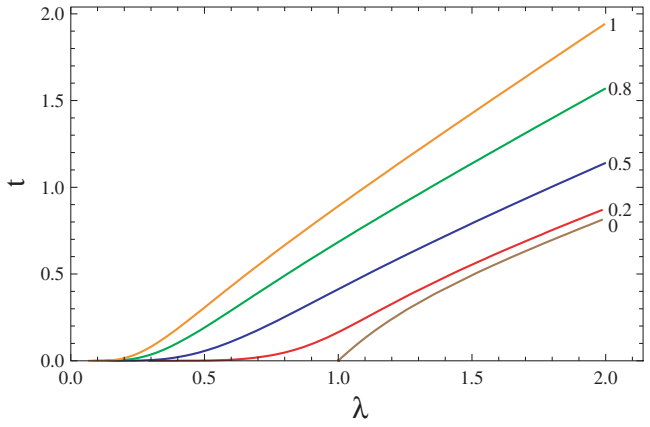

FIG. 2 (color online). Normalized critical temperature $t = 2T_c/\xi_m$ as a function of the interaction constant λ for various doping levels $|\mu|/\xi_m$. The quantum critical point is at $\lambda = 1$ and $|\mu| = 0$.

the current $\mathbf{j} = e\mu\mathbf{k}_s/4\pi\hbar$ is proportional to $|\mu| \propto \sqrt{n}$, where n is the density of free carriers provided by doping. Near the quantum critical point when $T \ll \xi_m$, the current is determined by the superconducting gap itself. Indeed, for zero doping, Eq. (14) yields

$$\Lambda = |\Delta| \tanh(|\Delta|/2T). \tag{15}$$

For low temperatures $T \ll |\Delta|$, we have $\mathbf{j} = e|\Delta|\mathbf{k}_s/4\pi\hbar$.

Note that the supercurrent is finite at $T = 0$ as distinct from the result of Ref. [10], where a vanishing supercurrent was found for $T \to 0$, $\mu = 0$. We believe that the disagreement comes from the fact that a formally diverging expression for the supercurrent was used in the cited work [see Eq. (67) of Ref. [10]]. On the contrary, integration over $d\xi_{\mathbf{p}}$ in Eq. (14) converges.

By modifying the self-consistency equation (3) to account for the current-carrying states, one can derive both the expression for the kinetic energy and the Ginzburg-Landau equation. Here the expansion should be done up to second order in $\mathbf{k}_s$, keeping in mind that $\tilde{\xi}_{\mathbf{p}} = \xi_{\mathbf{p}} + \delta\xi_{\mathbf{p}}$, where $\delta\xi_{\mathbf{p}} = (\hbar^2 k_i k_k/8)(\partial^2\xi_{\mathbf{p}}/\partial p_i \partial p_k)$ should be included as well. Indeed, in our case $p \sim (\xi_{\mathbf{p}} + \mu)/v_F$, which gives $\delta\xi_{\mathbf{p}}/\xi_{\mathbf{p}} \sim E_D^2/\xi_{\mathbf{p}}^2$ for zero doping. By calculating the kinetic energy, we recover Eq. (14), which provides an independent verification of the expression for supercurrent. The Ginzburg-Landau equation

$$\alpha\Delta - \beta|\Delta|^2\Delta - \gamma\mathbf{k}_s^2\Delta = 0$$

has a standard form; the coefficients are

$$\alpha = 2(T_c - T)\ln 2, \qquad \beta = 1/4T_c, \qquad \gamma = v_F^2/16T_c \tag{16}$$

in the case $\mu = 0$ and $\lambda - 1 \ll 1$, while

$$\alpha = |\mu|\frac{T_c - T}{T_c}, \qquad \beta = \frac{7\zeta(3)|\mu|}{8\pi^2 T_c^2}, \qquad \gamma = \frac{7\zeta(3)|\mu|v_F^2}{32\pi^2 T^2}$$

for the weak-coupling limit. The expression for γ in Eq. (16) leads to the same supercurrent as obtained from Eq. (13).

Characteristic lengths scales.—The coherence length in this model has the usual form $\xi_0 \sim \hbar v_F/\Delta$. For a layer of thickness d, the London penetration length at $T = 0$ is

$$\lambda_L^{-2} = 2e^2\Lambda/\hbar^2 c^2 d.$$

It diverges near the quantum critical point $\lambda \to 1$, $\mu \to 0$. For the undoped case, $\lambda_L = (\Phi_0/\pi)\sqrt{d/2|\Delta|}$, where $\Phi_0 = \pi\hbar c/e$ is the magnetic-flux quantum. Close to the critical temperature, $\lambda_L = (\Phi_0/\pi|\Delta|)\sqrt{T_c d}$. Similarly to conventional superconductors, the Ginzburg-Landau parameter $\kappa = \lambda_L/\xi_0$, which characterizes the type of superconductivity, has only a weak dependence on temperature: $\kappa \sim (c/v_F)\sqrt{T_c d/e^2}$. For typical values $v_F = 10^8$ cm/s, $d = 10^{-7}$ cm, and $T_c \sim 1$ K, the Ginzburg-Landau parameter is on the border between the two types: $\kappa \sim 1$. Therefore, close to the quantum critical point where $T_c \to 0$, the superconductivity definitely becomes of type I.

To summarize, we have calculated the critical temperature, the superconducting gap, and the supercurrent as functions of the doping level and of the interaction strength for an s-wave pairing within the BCS model. The superconducting transition in undoped graphene has a quantum critical point with respect to the interaction strength, which disappears for any finite doping level such that a finite critical temperature exists for any weak pairing interaction. The magnitude of the supercurrent is drastically affected by the presence of the Dirac point, which leads to nontrivial behavior of the characteristic length scales (penetration depth and coherence length) that determine the critical magnetic fields.

We thank Y. Kopelevich and V. Eltsov for stimulating discussions and A. Castro Neto for drawing our attention to Ref. [10]. This work was supported by the Forscheimer Foundation of the Hebrew University of Jerusalem, by the Academy of Finland (Grant No. 213496, Finnish Programme for Centers of Excellence in Research 2002–2007/2006–2011), by the ULTI program under EU Contract No. RITA-CT-2003-505313, and by the Russian Foundation for Basic Research Grant No. 06-02-16002.

[1] P. R. Wallace, Phys. Rev. **71**, 622 (1947).
[2] I. A. Luk'yanchuk and Y. Kopelevich, Phys. Rev. Lett. **93**, 166402 (2004).
[3] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature (London) **438**, 197 (2005).
[4] Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, Nature (London) **438**, 201 (2005).
[5] C. W. J. Beenakker, Phys. Rev. Lett. **97**, 067007 (2006).
[6] R. R. da Silva, J. H. S. Torres, and Y. Kopelevich, Phys. Rev. Lett. **87**, 147001 (2001).
[7] Y. Kopelevich, S. Moehlecke, and R. R. da Silva, in *Carbon Based Magnetism*, edited by T. Makarova and F. Palacio (Elsevier Science, New York, 2006), Chap. 18.
[8] B. Uchoa and A. H. Castro Neto, Phys. Rev. Lett. **98**, 146801 (2007).
[9] A. M. Black-Schaffer and S. Doniach, Phys. Rev. B **75**, 134512 (2007).
[10] B. Uchoa, G. G. Cabrera, and A. H. Castro Neto, Phys. Rev. B **71**, 184509 (2005).
[11] C. Honerkamp, Phys. Rev. Lett. **100**, 146404 (2008).
[12] E. C. Marino and Lizardo H. C. M. Nunes, Nucl. Phys. **B741**, 404 (2006); Physica (Amsterdam) **460C–462C**, 1101 (2007); Nucl. Phys. **B769**, 275 (2007).
[13] E. Zhao and A. Paramekanti, Phys. Rev. Lett. **97**, 230404 (2006).
[14] A. H. Castro Neto, F. Guinea, N. M. Peres, K. S. Novoselov, and A. K. Geim, arXiv:0709.1163v2.
[15] K. Sasaki, J. Jiang, R. Saito, S. Onari, and Y. Tanaka, J. Phys. Soc. Jpn. **76**, 033702 (2007).